

## UPPER ATMOSPHERE RESEARCH: REACTION RATE AND OPTICAL MEASUREMENTS

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## Abstract of Research Objectives

The objective of this research program is to provide photochemical, kinetic and spectroscopic information necessary for photochemical models of the Earth's upper atmosphere and to examine reactions or reactants not presently in the models to either confirm the correctness of their exclusion or provide evidence to justify future inclusion in the models. New initiatives are being taken in technique development (many of them laser based) and in the application of established techniques to address gaps in the photochemical/kinetic data base, as well as to provide increasingly reliable information.

## SUMMARY OF PROGRESS AND RESULTS

1. Reaction Rates and Reaction Products

The reactions of the hydroxymethyl radical with  $O_2$ , NO and  $NO_2$  have been studied in a discharge flow system as a function of temperature; formaldehyde ( $H_2CO$ ) was identified as a product for all three reactions. The results at 298 K for  $O_2$ , NO and  $NO_2$  respectively are:  $k_1 = 8.6 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ ,  $k_2 = 2.2 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$  and  $k_3 = 8.3 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ . The rate constants at mid stratospheric temperatures (220 K) are 2 to 3 times lower than at 298 K. A chemical link between natural and anthropogenic bromine species and ozone depletion in the Arctic atmosphere has recently been suggested. We have now examined the reaction  $Br + C_2H_4$  and the result obtained was  $k_4 = 1.6 \times 10^{-15} \text{ cm}^3 \text{ s}^{-1}$  independent of temperature (268-423 K) and total pressure (15-400 Torr Argon). In the presence of up to 2 Torr  $O_2$ ,  $k_4$  increased by an order of magnitude. At a fixed  $O_2$  concentration (0.75 Torr),  $k_4$  increased by a factor of 3 when total pressure was increased from 10 to 800 Torr Argon.

We have initiated a temperature study of the reaction of Cl with  $CH_3CHO$ , an intermediate in the atmospheric oxidation of  $C_2$  hydrocarbons. The reactions of Cl with oxygenated hydrocarbons have generally not been as well studied as those with the hydrocarbons themselves. The results obtained were  $k_5$  (298 K) =  $6.5 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  and  $k_5$  (210 K) =  $7.1 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ . Work is in progress at  $T > 298 \text{ K}$ . This is the first direct and absolute study of this reaction but it is consistent with previous indirect and/or relative studies at 298 K.

Collaborative work was also performed with Prof. D. Gutman (then at Illinois Institute of Technology) on the reaction  $Br + i-C_4H_{10} \rightleftharpoons HBr + t-C_4H_9$  in both directions to obtain thermochemical properties such as the heat of formation for hydrocarbon free radicals. Also, collaboration with Dr. T. Wallington (Ford Research Division) on the pressure dependence of the reaction of Cl with  $C_2H_2$  and  $C_2H_4$  showed good agreement with our previous direct results on  $Cl + C_2H_2$  but the more extensive pressure range of the new data leads to a larger value for  $k_{\infty}$  at 298 K ( $2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ ).

Finally, we replaced the data collection and analysis system for the flash photolysis apparatus, the discharge flow system was modified to include photoionization detection, and our move to a new laboratory was completed.

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## 2. Optical and Spectroscopic Measurements

For the past several years we have conducted an experimental program to develop intracavity laser absorption spectroscopy for application to chemical problems related to stratospheric research. For  $\text{NO}_2$  the absorption linewidth is narrower than the laser bandwidth and the technique gives quantitative results, if the data are represented by a modified Beer's law that is based on a measure of the apparent absorbance. Enhancements as high as 23,000 over conventional absorption were obtained. The same apparatus was then used to demonstrate the utility of the technique by measuring the rate for the reaction of NO with  $\text{O}_2$  and the result was in excellent agreement with the recommended value.

Another study examined the case for which the absorption linewidth is broader than the laser bandwidth. Ozone ( $\text{O}_3$ ) was used as the absorber and the experiments performed at 630 nm, corresponding to absorption in the Chappuis bands. It was determined that the absorption was best represented by absorptance ( $\Delta I/I_0$ ) and followed a modified Beer's law. Enhancements in the range  $10^2$  to  $10^3$  were obtained, because mode competition does not play a role here. Thus, we determined that mode competition accounts for a factor of 10 to  $10^2$  in the enhancement for the narrowband case.

In the next phase  $\text{O}_3$  was dissociated at 254 nm, producing O atoms with a quantum yield near unity. Intracavity absorption at 630 nm, corresponding to the  $^1\text{D} \leftarrow ^3\text{P}$  transition, was clearly evident.  $\text{O}(^3\text{P})$  atoms were directly and  $\text{O}(^1\text{D})$  atoms in-directly detected in this system. This represents the first detection by intracavity laser absorption of O atoms produced by photolysis.

To investigate the utility of quasi-cw operation for application to time resolved experiments, a new experimental arrangement was implemented. This set up was used to measure weak absorption of combination bands in water vapor present as humidity in the room air. The absorbance was found to vary linearly with generation time for  $t \leq 170 \mu\text{sec}$ . This study indicates that this method can be used effectively to follow fast reactions of radicals.

Significant improvements have been made in both our facilities and the experiment. Our entire laboratory was moved to a recently completed laboratory wing that was specifically designed for our use. The intracavity dye laser absorption spectrometer has been significantly upgraded with the incorporation of a 1.26 m microprocessor-controlled spectrometer. An electro-optic modulator has been incorporated into the system for quasi-cw operation.

### JOURNAL PUBLICATIONS

"Temperature Dependence for the Absolute Rate Constant for the Reaction  $\text{CH}_2\text{OH} + \text{O}_2 \longrightarrow \text{HO}_2 + \text{H}_2\text{CO}$  from 215 to 300 K," F. L. Nesbitt, W. A. Payne and L. J. Stief, J. Phys. Chem., 92, 4030 (1988).

"Kinetics and Thermochemistry of the  $t\text{-C}_4\text{H}_9$  Radical. Study of the Equilibrium  $t\text{-C}_4\text{H}_9 + \text{HBr} \rightleftharpoons i\text{-C}_4\text{H}_9 + \text{Br}$ ," J. J. Russell, J. A. Seetula, R. S. Timonen, D. Gutman and D. F. Nava, J. Amer. Chem. Soc., 110, 3084 (1988).

"Kinetic Studies of the Reaction of the Hydroxymethyl Radical with NO and  $\text{NO}_2$ ," F. L. Nesbitt, W. A. Payne and L. J. Stief, J. Phys. Chem., 93, 5158 (1989).

"Rate Determination for the Reaction  $\text{NO} + \text{NO} + \text{O}_2$  Using Intracavity Dye Laser Absorption Spectroscopy," W. D. Brobst and J. E. Allen, Jr., submitted to Int. J. Chem. Kin., (1989).

"Intracavity Dye Laser Absorption Spectroscopy with a Broadband Absorber: Detection of  $\text{O}_3$  in the Chappuis Bands," W. D. Brobst and J. E. Allen, Jr., submitted to Appl. Opt., (1989).

## CHEMICAL KINETICS OF THE UPPER ATMOSPHERE

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### Objectives

To obtain direct measurements of rate constants and temperature dependences for reactions of  $\text{HO}_x$ ,  $\text{NO}_x$ ,  $\text{ClO}_x$ ,  $\text{BrO}_x$ , and  $\text{RO}_x$  which are relevant to stratospheric chemistry, including both homogeneous and heterogeneous reactions on particle surfaces which are important in both the polar and normal stratospheric regions.

### Progress

Measurements were made of the sticking coefficients of  $\text{HCl}$ ,  $\text{H}_2\text{O}$ ,  $\text{HNO}_3$ ,  $\text{NO}$ ,  $\text{NO}_2$ , and  $\text{O}_3$  on ice surfaces. These measurements were accomplished by a flow reactor combined with mass spectral detection (FR/MS). Measurements were made of the reaction probabilities of  $\text{ClONO}_2 + \text{HCl}$  and  $\text{ClONO}_2 + \text{H}_2\text{O}$  reactions on ice surfaces by the FR/MS technique. The reaction probabilities of  $\text{N}_2\text{O}_5 + \text{HCl}$  and  $\text{N}_2\text{O}_5 + \text{H}_2\text{O}$  on ice surfaces were measured by the FR/MS technique. The solubility of  $\text{HCl}$  in acid ices was measured by a diode laser/mass spectral method. Temperature dependence of the  $\text{OH} + \text{HO}_2$  reaction was measured by the discharge flow/resonance fluorescence method.

### Publications

1. "Kinetics of the Reaction  $\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$  from 254 to 382K", L. F. Keyser, J. Phys. Chem. 92, 1193, (1988).
2. "Laboratory Studies of Heterogeneous Reactions and Thermodynamic Properties of Acid-Ice Surfaces Important in the Polar Stratosphere", L. F. Keyser, S. B. Moore, and M. T. Leu, 18th Informal Conference on Photochemistry, 1989.
3. "Laboratory Studies of Sticking Coefficients and Heterogeneous Reactions Important in the Antarctic Stratosphere", M. T. Leu, Geophys. Res. Lett. 15, 17 (1988).
4. "Heterogeneous Reactions of  $\text{N}_2\text{O}_5$  with  $\text{HCl}$  and  $\text{H}_2\text{O}$  on Ice Surfaces: Implications for Antarctic Ozone Depletion", M. T. Leu, Geophys. Res. Lett. 15, 851, (1988).
5. "Rate Constants for Reactions between Atmospheric Reservoir Species II.  $\text{H}_2\text{O}$ ", S. Hatakeyama and M. T. Leu, J. Phys. Chem., in press, 1989.
6. "Rate Constants for Reactions between Atmospheric Species I.  $\text{HCl}$ ", M. T. Leu, S. Hatakeyama, and K. Y. Hsu, J. Phys. Chem., in press (1989).

## LABORATORY INVESTIGATIONS OF STRATOSPHERIC BROMINE CHEMISTRY

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### Research Objectives

The initial objectives of this task were to employ state-of-the-art experimental methods to investigate the kinetics of a number of reactions of the active bromine species Br and BrO which are of proven or potential importance in stratospheric chemistry, and to investigate the photochemistry of the important bromine reservoir species BrONO<sub>2</sub> (bromine nitrate). Subsequently, we expanded our objectives to include studies of the kinetics and thermochemistry of several weakly bound chlorine-containing species which may play a role in stratospheric ClO<sub>x</sub> chemistry.

### Progress and Results

Reactions studied during 1988 and 1989 are listed below along with a summary of results and a few pertinent comments.

- (1)  $\text{Br} + \text{O}_3 \longrightarrow \text{BrO} + \text{O}_2$   
T dependence of  $k_1$ , 195-392K; Good agreement with previous studies.
- (2)  $\text{Cl} + \text{O}_3 \longrightarrow \text{ClO} + \text{O}_2$   
T dependence of  $k_2$ , 189-385K; Non-Arrhenius behavior observed;  $k_2$  faster than previously thought at low T.
- (3)  $\text{Cl} + \text{O}_2 + \text{O}_2 \rightleftharpoons \text{ClOO} + \text{O}_2$   
 $k_3$ ,  $k_{-3}$ ,  $K_{\text{eq}}$  determined at T = 185K, P = 15-40 Torr; Third law method used to obtain ClOO heat of formation;  $k_3$  faster than previously thought; ClOO less stable than previously thought.
- (4)  $\text{Cl} + \text{CO} + \text{M} \rightleftharpoons \text{ClCO} + \text{M}$ , M = N<sub>2</sub>, CO, Ar, CO<sub>2</sub>  
T & P dependence of  $k_4$ ,  $k_{-4}$ ,  $K_{\text{eq}}$ , 185-260K; Second and third law methods used to obtain ClCO heat of formation; ClCO more stable than previously thought.
- (5)  $\text{Cl} + \text{CS}_2 + \text{M} \rightleftharpoons \text{CS}_2\text{Cl} + \text{M}$ , M = N<sub>2</sub>, O<sub>2</sub>  
T & P dependence of  $k_5$ ,  $k_{-5}$ ,  $K_{\text{eq}}$ , 193-258K; Second law method used to obtain CS<sub>2</sub>Cl heat of formation; CS<sub>2</sub>Cl found to be unreactive toward O<sub>2</sub>.
- (6)  $\text{Cl} + \text{COS} + \text{N}_2 \rightleftharpoons \text{COSCl} + \text{N}_2$   
Evidence of equilibrium between Cl and COSCl sought at low T (190K); No reaction observed.
- (7)  $\text{Br} + \text{CH}_3\text{CHO} \longrightarrow \text{CH}_3\text{CO} + \text{HBr}$   
First study T dependence of  $k_1$ , 255-400K;  $k_7$ (298K) found to be 25% faster than previously thought; 298K rate coefficient for CH<sub>3</sub>CO + Br<sub>2</sub> → CH<sub>3</sub>CBrO + Br also determined.

- (8)  $O + Br_2 \longrightarrow BrO + Br$   
 $k_8$  independent of T, 255-350K, 40% faster than previously thought.
- (9)  $O + HBr \longrightarrow OH + Br$   
 T dependence of  $k_9$ , 250-402K; Good agreement with previous studies;  
 Confirmation of theoretically predicted non-Arrhenius behavior.
- (10)  $Cl + Br_2 \longrightarrow BrCl + Br$   
 $k_{10}$  nearly gas kinetic, virtually independent of T, 298-401K.
- (11)  $Cl + HBr \longrightarrow HCl + Br$   
 T-dependence of  $k_{11}$ , 257-414K; Poor agreement with previous studies.
- (12)  $Br + NO_2 + M \rightleftharpoons BrNO_2 + M$ , M = He, Ar, H<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub>, CF<sub>4</sub>  
 T- and P-dependence of irreversible association reaction, 259-346K,  
 12.5-700 Torr; BrNO<sub>2</sub> dissociation observed at T > 350K allowing  
 determination of BrNO<sub>2</sub> heat of formation; Fall-off parameters  
 determined; First T-dependence study and first study to investigate  
 fall-off regime.
- (13)  $BrO + NO_2 + N_2 \longrightarrow BrONO_2 + N_2$   
 T- and P-dependence, 245-346K, 16-800 Torr; Good agreement with previous  
 study at 298K; T-dependence of fall-off parameters determined.
- (14)  $BrONO_2 + h\nu \longrightarrow \text{products}$   
 Study initiated during summer of 1989.

#### Journal Publications

- "Temperature-Dependent Absorption Cross Sections for Hydrogen Peroxide Vapor," J. M. Nicovich and P. H. Wine, J. Geophys. Res. 93, 2417 (1988).
- "Kinetics of the Reactions of F(<sup>2</sup>P) and Cl(<sup>2</sup>P) with HNO<sub>3</sub>," P. H. Wine, J. R. Wells, and J. M. Nicovich, J. Phys. Chem. 92, 2223 (1988).
- "Pulsed Laser Photolysis Kinetics Study of the O(<sup>3</sup>P) + ClO Reaction," J. M. Nicovich, P. H. Wine, and A. R. Ravishankara, J. Chem. Phys. 89, 5670 (1988).
- "Kinetics of the Br<sub>2</sub> - CH<sub>3</sub>CHO Photochemical Chain Reaction," J. M. Nicovich, C. J. Shackelford and P. H. Wine, J. Photochem. Photobiol., A:Chem., submitted, March 1989.
- "Kinetics of Reversible Adduct Formation in the Reactions of Cl(<sup>2</sup>P<sub>J</sub>) with CS<sub>2</sub> and COS," J. M. Nicovich, C. J. Shackelford, and P. H. Wine, J. Phys. Chem., submitted, May, 1989.
- "Kinetics of the Reactions of Cl(<sup>2</sup>P<sub>J</sub>) and Br(<sup>2</sup>P<sub>3/2</sub>) with O<sub>3</sub>," J. M. Nicovich, K. D. Kreutter, and P. H. Wine, Int. J. Chem. Kinet., submitted, June, 1989.
- "Kinetics of the Reactions of O(<sup>3</sup>P) and Cl(<sup>2</sup>P) with HBr and Br<sub>2</sub>," J. M. Nicovich and P. H. Wine, Int. J. Chem. Kinet., submitted, July, 1989.
- "Formation-Dissociation Kinetics and Thermochemistry of the ClCO Radical," J. M. Nicovich, K. D. Kreutter, and P. H. Wine, manuscript in preparation for submission to J. Phys. Chem., Second International Conference on Chemical Kinetics special issue, September, 1989.

## A MOLECULAR BEAM MASS SPECTROMETRIC STUDY OF THE FORMATION AND PHOTOLYSIS OF C10 DIMER

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### Research Objectives

The dimer of C10 radical has been proposed as a key intermediate in the catalytic destruction of ozone in the antarctic stratosphere. To date evidence for the existence of this transient species has come from infrared and ultraviolet spectroscopic observations in laboratory studies. The objectives of this research program are the identification of C10 dimer by molecular beam mass spectrometry, the measurement of the rate of formation of the dimer over a wide range of temperatures and pressures, and the elucidation of the photochemistry of the dimer.

### Summary of Progress and Results

The objective of the first phase of this work was the determination of whether the C10 dimer could be measured mass spectrometrically in preparation for studies of its kinetic and photochemical behavior. In this work the dimer of C10 was generated in four different chemical systems by the combination of C10 radicals in a simple flow reactor operated at total pressures ranging from 5 to 200 torr, temperatures from -40° to 20°C and residence times from 0.04 to 2 sec. The C10 radicals were produced by the reaction of Cl atoms, which were generated by photolysis of Cl<sub>2</sub> with C10<sub>2</sub>, O<sub>2</sub>, or Cl<sub>2</sub>O and by the reaction of thermally generated Cl atoms with C10<sub>2</sub>. The flow reactor was interfaced to a molecular beam mass spectrometric system which incorporated both a large magnetic mass spectrometer with high resolution capabilities and a quadrupole mass spectrometer, and which utilized beam modulation and phase sensitive detection. This system, which was optimized for operation at pressures up to 1 atm and which had a detection limit of better than 1 ppb, was used to obtain mass spectra of the reaction products at an ionizing energy of 20 eV. In addition to the expected signals for reactants and C10 radicals, strong signals were also obtained at m/e = 102, 104 and 106. These ions were assigned to the dimer of C10 based on: (1) The mass to charge ratio, (2) the excellent agreement between the observed and calculated isotope ratios, (3) the fact that the ions were only observed in the presence of light in the photolysis experiments or when the furnace temperature was great enough to dissociate Cl<sub>2</sub> in the thermal experiments, and (4) the weak dependence of the ratio of C10 dimer to C10 on reactor pressure, which suggested that it was not being produced in the initial beam forming process during sampling.

The mass spectrometric identification of the ClO dimer was further supported by time-of-flight velocity analyses. Velocity distributions were obtained for the neutral precursors of the dimer of ClO and for several other species. These distributions showed that the neutral precursor of  $\text{Cl}_2\text{O}_2^+$  has a nominal mass of 102 amu and that  $\text{Cl}_2\text{O}_2^+$  cannot be a fragment from a significantly larger molecule, such as one containing one or more additional chlorine or oxygen atoms.

The results obtained to date show that ClO dimer can be readily measured by molecular beam mass spectrometry. It should therefore be possible to utilize this technique to make detailed measurements of the kinetics of formation and photochemical behavior of the dimer.

# LABORATORY STUDIES OF HETEROGENEOUS PROCESSES IN THE ATMOSPHERE

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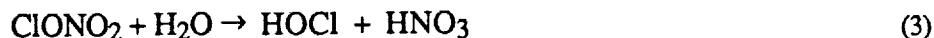
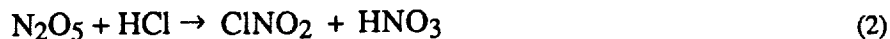
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## RESEARCH OBJECTIVES

Heterogeneous reactions on the surfaces of polar stratospheric clouds (PSCs) are now recognized to play a central role in the dramatic yearly occurrence of the Antarctic 'ozone hole'. In addition, heterogeneous reactions on normal stratospheric particulate may be important in the global ozone cycle. The goal of this research program is to identify and quantify heterogeneous processes that may have an impact on the stratospheric ozone layer. The surfaces of interest for stratospheric chemistry include ice, concentrated frozen mixtures of nitric acid and ice, and concentrated liquid solutions of sulfuric acid and water.

## SUMMARY OF PROGRESS AND RESULTS

**Heterogeneous interactions on model PSC surfaces.** A Knudsen cell flow reactor was used to study the heterogeneous reactions (1-4) of chlorine nitrate ( $\text{ClONO}_2$ ) and



dinitrogen pentoxide ( $\text{N}_2\text{O}_5$ ) on ice surfaces representative of type II PSCs. All four reactions occurred readily on laboratory ice surfaces at 185 K. Reactions 1,2 and 3 formed gaseous products  $\text{Cl}_2$ ,  $\text{ClNO}_2$  and  $\text{HOCl}$ , respectively. All of these molecules could be readily photolyzed in the Antarctic spring sunlight to form active chlorine for catalytic ozone destruction cycles. Surface evaporation studies showed that reactions 1-4 all resulted in the formation of  $\text{HNO}_3$  condensed in the ice. Nitric acid condensed in PSCs



would provide a sink for odd nitrogen during the polar winter, a requirement in nearly all models of Antarctic ozone depletion.

**Heterogeneous processes on sulfuric acid surfaces.** The heterogeneous interactions of  $\text{ClONO}_2$ ,  $\text{HCl}$  and  $\text{HNO}_3$  were studied on sulfuric acid surfaces representative of global stratospheric particulate. The surfaces were composed of 65-75% sulfuric acid and were held at temperatures in the range 210 to 230 K. Heterogeneous loss, but not reaction, of  $\text{HNO}_3$  and  $\text{HCl}$  occurred on these surfaces. Chlorine nitrate reacted on the cold sulfuric acid surfaces, producing gas phase  $\text{HOCl}$ . Nitric acid was formed partitioned between the gas and condensed phases. Chlorine nitrate also reacted with  $\text{HCl}$  dissolved in the more dilute sulfuric acid solutions, forming gaseous  $\text{Cl}_2$ . In all cases studied, the sticking and/or reactions coefficients were much larger for the more dilute sulfuric acid solutions.

#### JOURNAL PUBLICATIONS

1. "Reaction of chlorine nitrate with hydrogen chloride and water at Antarctic stratospheric temperatures", M.A. Tolbert, M.J. Rossi, R. Malhotra and D.M. Golden, *Science* 238, 1258-1260, 1987.
2. "Antarctic ozone depletion chemistry: reactions of  $\text{N}_2\text{O}_5$  with  $\text{H}_2\text{O}$  and  $\text{HCl}$  on Ice Surfaces", M.A. Tolbert, M.J. Rossi and D.M. Golden, *Science* 240, 1018-1021, 1988.
3. "Heterogeneous interactions of chlorine nitrate, hydrogen chloride, and nitric acid with sulfuric acid surfaces at stratospheric temperatures", M.A. Tolbert, M.J. Rossi and D.M. Golden, *Geophys. Res. Lett.* 15, 847-850, 1988.

# PHOTOCHEMICAL AND KINETIC MEASUREMENTS OF ATMOSPHERIC CONSTITUENTS VIS-A-VIS THEIR ROLE IN CONTROLLING STRATOSPHERIC OZONE

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## Research Objectives

This task focuses on the elucidation of stratospheric photochemical kinetics through laboratory studies of select chemical reaction systems. Experiments are designed and conducted to determine the temperature and pressure dependencies of rate constants and to infer the mechanisms for those processes important in the modeling of atmospheric chemistry. While the research emphasis is directed towards an assessment of the effects of anthropogenic activity on stratospheric chemical composition, certain predominantly tropospheric reaction systems are also investigated because of their influence on chemical transport to the stratosphere and/or their mechanistic similarities to stratospheric processes. Under this task, the principal investigator also serves as a member of the NASA Panel for Data Evaluation and assists in the annual preparation of a tabulation of evaluated kinetic and photochemical data applicable to atmospheric modeling.

## Summary of Progress and Results

Laboratory activities under this task during 1988 and 1989 fall into two general experimental categories: a) peroxy radical studies conducted via flash photolysis uv absorption spectroscopy (FPAS) and b) hydroxyl radical kinetic investigations performed using the flash photolysis resonance fluorescence (FPRF) technique. Accomplishments under both categories include:

FPAS: UV Absorption Cross-Sections for  $\text{CH}_3\text{O}_2$ ,  $\text{CH}_2\text{ClO}_2$ ,  $\text{CH}_2\text{FO}_2$ ,  $\text{CH}_2\text{ClCH}_2\text{O}_2$ ,  $\text{CH}_3\text{OCH}_2\text{O}_2$ , and  $\text{C}(\text{CH}_3)_3\text{CH}_2\text{O}_2$ .

$\text{CH}_2\text{ClO}_2 + \text{CH}_2\text{ClO}_2$  Kinetics - Temperature dependence of the rate constant.

$\text{CH}_2\text{FO}_2 + \text{CH}_2\text{FO}_2$  Kinetics - Temperature dependence of the rate constant.

$\text{CH}_2\text{ClCH}_2\text{O}_2 + \text{CH}_2\text{ClCH}_2\text{O}_2$  Kinetics - Temperature dependence of the rate constant.

$\text{CH}_3\text{OCH}_2\text{O}_2 + \text{CH}_3\text{OCH}_2\text{O}_2$  Kinetics - Temperature and pressure dependence of the rate constant.

$\text{C}(\text{CH}_3)_3\text{CH}_2\text{O}_2 + \text{C}(\text{CH}_3)_3\text{CH}_2\text{O}_2$  Kinetics - Temperature and pressure dependence of the rate constant.

CF<sub>2</sub>ClO<sub>2</sub> + Cl Reaction - Modeling estimate of the rate constant at room temperature.

**FPRF:** OH Reaction Kinetics - Temperature dependencies of the rate constants for the reactions with alcohol and ether fuel additives, carboxylic acids, C<sub>5</sub> through C<sub>7</sub> aliphatic alcohols and ethers, cyclic ketones and diones, difunctional organic oxygenates, cyclic ethers, aliphatic polyethers, and chlorofluoroethanes.

### Journal Publications

1. "The Gas Phase Reactions of Hydroxyl Radicals with the Fuel Additives Methyl-t-Butyl Ether and t-Butyl Alcohol over the Temperature Range 240 - 440 K", T. J. Wallington, P. Dagaut, R. Liu, and M. J. Kurylo, *Environ. Sci. and Tech.* **22**, 842 (1988).
2. "The Gas Phase Reactions of Hydroxyl Radicals with a Series of Carboxylic Acids over the Temperature Range 240 - 440 K", P. Dagaut, T. J. Wallington, R. Liu, and M. J. Kurylo, *Int. J. Chem. Kinet.* **20**, 331 (1988).
3. "Rate Constants for the Gas Phase Reaction of OH Radicals with C<sub>5</sub> through C<sub>7</sub> Aliphatic Alcohols and Ethers: Predicted and Experimental Values", T. J. Wallington, P. Dagaut, R. Liu, and M. J. Kurylo, *Int. J. Chem. Kinet.*, **20**, 541 (1988).
4. "A Kinetics Investigation of the Gas Phase Reaction of OH Radicals with Cyclic Ketones and Diones: Mechanistic Insights", P. Dagaut, T. J. Wallington, R. Liu, and M. J. Kurylo, *J. Phys. Chem.*, **92**, 4375 (1988).
5. "A Correlation Between Gas Phase and Solution Phase Reactivities of OH Radicals towards Saturated Organic Compounds", T. J. Wallington, P. Dagaut, and M. J. Kurylo, *J. Phys. Chem.* **92**, 5024 (1988).
6. "The UV Absorption Spectra and Kinetics of the Self Reactions of CH<sub>2</sub>ClO<sub>2</sub> and CH<sub>2</sub>FO<sub>2</sub> Radicals in the Gas Phase", P. Dagaut, T. J. Wallington, and M. J. Kurylo, *Int. J. Chem. Kinet.* **20**, 815 (1988).
7. "A Flash Photolysis Kinetic Spectroscopy Investigation of the Absorption Spectrum and Self-Reaction of C<sub>2</sub>H<sub>4</sub>ClO<sub>2</sub> Radicals in the Gas Phase", *Chem. Phys. Lett.* **146**, 589 (1988).
8. "Group Reactivities in the Gas Phase Reactions of Hydroxyl Radicals with Ethers", *Acta Physico-Chimica Sinica* **5**, 210 (1989).
9. "Gas Phase Studies of Substituted Methyl Peroxy Radicals: The UV Absorption Spectrum and Self-Reaction Kinetics of CH<sub>3</sub>OCH<sub>2</sub>O<sub>2</sub>; The Reaction of CF<sub>2</sub>ClO<sub>2</sub> with Cl Atoms", P. Dagaut, T. J. Wallington, and M. J. Kurylo, *J. Photochem. and Photobiol., A: Chem.* **48**, 187 (1989).
10. "Kinetic Measurements of the Gas Phase Reactions of OH Radicals with Hydroxyethers, Hydroxyketones, and Ketoethers", P. Dagaut, R. Liu, T. J. Wallington, and M. J. Kurylo, *J. Phys. Chem.*, **93**, xxxx (1989).

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12. "A Flash Photolysis Resonance Fluorescence Investigation of the Gas Phase Reactions of Hydroxyl Radicals with a Series of Cyclic Ethers", P. Dagaut, R. Liu, T. J. Wallington, and M. J. Kurylo, *J. Phys. Chem.*, in press (1989).
13. "The UV Absorption Spectra of Methylperoxy Radicals in the Gas Phase: A Reinvestigation", P. Dagaut and M. J. Kurylo, *J. Photochem. and Photobiol., A: Chem.*, in press (1989).
14. "A Flash Photolysis Investigation of the Gas Phase UV Absorption Spectrum and Self-Reaction Kinetics of the Neopentylperoxy Radical", *Int. J. Chem. Kinet.*, submitted for publication (1989).
15. "An Evaluation of the Gas Phase Reaction Rates of OH Radicals and O(<sup>1</sup>D) Atoms with Select Chlorofluorocarbons and Fluorocarbons", prepared for the Alternate Fluorocarbon Environmental Acceptability Study (AFEAS), UNEP/WMO Special Report (1989).
16. "A Flash Photolysis Resonance Fluorescence Investigation of the Reactions of OH Radicals with Chlorofluoroethanes", R. Liu, R. E. Huie, and M. J. Kurylo, *J. Phys. Chem.*, submitted for publication (1989).

## Biennial Report for NASA

### SPECTROSCOPIC STUDIES OF REACTION INTERMEDIATES AND PRODUCTS

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#### Research Objectives

This project involves spectroscopic studies of reaction rates, intermediates and products. A high resolution Fourier transform spectrometer and a linear photodiode array spectrometer are used to obtain IR, visible, and UV spectra of transient and stable species of atmospheric importance. Reaction rate constants are measured, reaction mechanisms are analyzed, and spectra and absorption cross sections are determined for stable and labile chemical species. The results obtained help reduce some of the uncertainties in stratospheric chemistry and provide spectroscopic data for laboratory and field measurements.

#### Progress and Results

##### 1) Antarctic Ozone Hole Chemistry

(a) The ultraviolet and infrared absorption cross sections of  $\text{Cl}_2\text{O}_2$  were measured by producing it via the reaction,  $\text{ClO} + \text{ClO} + \text{M} \rightarrow \text{Cl}_2\text{O}_2 + \text{M}$ . The  $\text{ClO}$  radical was produced by:  $\text{Cl} + \text{O}_3$ ,  $\text{Cl} + \text{Cl}_2\text{O}$ , or  $\text{Cl} + \text{OCIO}$  reaction. The UV absorption spectrum between 205 and 250 K was recorded over the 200 - 450 nm range with a diode array spectrometer. The infrared spectrum was recorded with a high resolution Fourier transform spectrometer. Both spectrometers were optically coupled to a fast flow multipass absorption cell to permit simultaneous IR and UV measurements on the same gas sample. The UV absorption spectrum of  $\text{Cl}_2\text{O}_2$  is a structureless continuum with a maxima at 245 nm and a long wavelength tail which extends out to 410 nm. The UV absorption cross section at 245 nm was measured to be  $(6.5 \pm 1.0) \times 10^{-18} \text{ cm}^2$ . Infrared absorption features centered at 570, 653, and  $750 \text{ cm}^{-1}$  were assigned to the  $\text{Cl}_2\text{O}_2$  molecule. The UV spectrum of  $\text{Cl}_2\text{O}_2$  allows the calculation of its photolytic lifetime in the atmosphere.

(b) The rate coefficient for the reaction which forms  $\text{Cl}_2\text{O}_2$ ,  $\text{ClO} + \text{ClO} + \text{M} \rightarrow \text{Cl}_2\text{O}_2 + \text{M}$ , was measured between 200 and 265 K in the pressure range of 25 to 600 Torr of He,  $\text{N}_2$ ,  $\text{O}_2$  and  $\text{SF}_6$ . The loss of  $\text{ClO}$  was monitored via UV absorption at 282.7 nm (9-0 band) using a monochromator or via UV absorption between 270 and 300 nm using a spectrometer/diode array system. The measured rate coefficients are lower than those published earlier and were carried out at or near Antarctic temperatures. Using this data more accurate ozone depletion calculations can be carried out.

(c) The UV absorption cross sections of  $\text{ClO}$  in the  $\text{A}^2\Pi \leftarrow \text{x}^2\Pi$ , system (225 to 325 nm) were measured as a function of temperature between 200 and 300 K. The cross section at the top of the continuum, 265 nm, was measured to be  $(5.33 \pm 0.50) \times 10^{-18} \text{ cm}^2$ , independent of temperature. The cross sections in the structured part, 270 - 300 nm, are very temperature and instrumental resolution dependent. These measurements provide necessary data for field and laboratory measurements of  $\text{ClO}$ .

##### 2 ) High Resolution IR Spectroscopy

###### (a) IR Line positions of $\text{HNO}_3$

High resolution measurements were made on the  $\nu_9$  band of  $\text{HNO}_3$  from 414 to  $500 \text{ cm}^{-1}$ . Over 2300 transitions were measured, assigned, and fit to obtain 15 rovibrational constants for the  $\nu_9 = 1$  state that reproduce the observed spectrum with a RMS deviation of  $0.0004 \text{ cm}^{-1}$ . The band center for  $\nu_9$  is at  $458.2287 \pm 0.0005 \text{ cm}^{-1}$ . These measurements provide data necessary to interpret atmospheric IR measurements of the  $\nu_9$  band of  $\text{HNO}_3$ .

(b) Fundamental IR intensities of ClO

The fundamental,  $v = 0 - 1$ , vibrational band intensity of the ClO radical was measured using a high resolution Fourier transform spectrometer (FTS) with calibrated flows of ClO. A source of systematic error in the use of the  $\text{Cl} + \text{O}_3$  reaction as a stoichiometric source of ClO was discovered. Our result on the band intensity is in general agreement with all other recent measurements except one.

Journal Publications:

High-Resolution Infrared Fourier Transform Spectroscopy of SO in the  $X^3\Sigma$  and  $a^1\Delta$  Electronic States, James B. Burkholder, Edward R. Lovejoy, Philip D. Hammer, Carleton J. Howard, and Masataka Mizushima, *J. Molecular Spectroscopy* **124**, 379 - 392, 1987.

High Resolution Fourier Transform Infrared Spectra of  $^{12}\text{C}^{32}\text{S}$ ,  $^{12}\text{C}^{33}\text{S}$ ,  $^{12}\text{C}^{34}\text{S}$ , and  $^{13}\text{C}^{32}\text{S}$ , James B. Burkholder, Edward R. Lovejoy, Philip D. Hammer, and Carleton J. Howard, *J. Molecular Spectroscopy* **124**, 450 - 457, 1987.

Fourier Transform Infrared Spectra of the  $\text{FO}_2$  Radical, A.R.W. McKellar, James B. Burkholder, Amitabha Sinha, and Carleton J. Howard, *J. Molecular Spectroscopy* **125**, 288 - 308, 1987.

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Fourier Transform Infrared Spectrum of the  $\nu_2$  Band of the  $\text{NH}_2$  Radical, James B. Burkholder, Carleton J. Howard, and A.R.W. McKellar, *J. Molecular Spectroscopy* **127**, 415 - 424, 1988.

High-Resolution Fourier Transform Infrared Spectroscopy of the CCl Radical ( $X^2\Pi_{3/2,1/2}$ ), James B. Burkholder, Amitabha Sinha, Philip D. Hammer, and Carleton J. Howard, *J. Molecular Spectroscopy* **127**, 61 - 69, 1988.

Fourier Transform Infrared Spectroscopy of the  $\text{BO}_2$  Radical, Arthur G. Maki, James B. Burkholder, Amitabha Sinha, and Carleton J. Howard, *J. Molecular Spectroscopy* **130**, 238 - 248, 1988.

High Resolution Study of FO Infrared Chemiluminescence, Philip D. Hammer, Amitabha Sinha, James B. Burkholder, and Carleton J. Howard, *J. Molecular Spectroscopy*, **129**, 99 - 118, 1988.

Spectroscopic Constants for the  $\nu_9$  Infrared Band of  $\text{HNO}_3$ , Aaron Goldman, James B. Burkholder, and Carleton J. Howard, *J. Molecular Spectroscopy*, **131**, 195 - 200, 1988.

High Resolution Fourier Transform Infrared Spectroscopy of the  $\text{N}_3$  Radical, Chris Brazier, Peter Bernath, James B. Burkholder, and Carleton J. Howard, *J. Chemical Physics*, **89**, 1762 - 1767, 1988.

High Resolution Fourier Transform Infrared Spectroscopy of the NS Radical, Amitabha Sinha, James B. Burkholder, Philip D. Hammer, and Carleton J. Howard, *J. Molecular Spectroscopy*, **130**, 466 - 469, 1988.

High Resolution Fourier Transform Infrared Spectroscopy of the HCO Radical, A.R.W. McKellar, James B. Burkholder, John Orlando, and Carleton J. Howard, *J. Molecular Spectroscopy*, **130**, 445 - 453, 1988.

Absorption Cross Sections of BrO between 312 and 385 nm at 298 and 223 K, A. Wahner, A.R. Ravishankara, S.P. Sander, and R.R. Friedl, *Chem. Phys. Lett.* **152**, 507 - 512, 1988

Infrared Line Strength Measurements of the ClO Radical, James B. Burkholder, Philip D. Hammer, Carleton J. Howard, and Aaron Goldman, *J. Geophysical Research*, **94**, D2, 2225 - 2234, 1989.

- A. Laboratory Measurements of Photolytic and Kinetic Data Affecting Atmospheric Ozone
- B. Tom G. Slanger, Molecular Physics Laboratory, SRI International, Menlo Park, CA.
- C. Research Objectives. The experimental part of the program has been directed towards an improved understanding of ozone photochemistry, as related to upper atmospheric issues. Apart from the well-publicized Antarctic ozone hole, there are other discrepancies that are found between what modelers predict for the ozone altitude profiles, and what is actually observed. At present, there is an excess amount of ozone in the upper stratosphere and lower mesosphere at temperate latitudes compared to modeling predictions, amounting to 50-100%. This is obviously a consequence of either an underestimation of sources, or an overestimation of losses. We have pursued the former hypotheses, and have shown that the role of vibrationally excited oxygen may be crucial in the photochemistry of the upper stratosphere.
- D. Progress and Results. The essence of the work carried out in 1988 has been to demonstrate that the atmosphere has an unexpected potential source of ozone which has not been included in current models. It has always been taken for granted that ozone itself cannot be an ozone source, and that it can only be generated by oxygen photodissociation.

We have shown in the laboratory that irradiation of a dilute mixture of ozone in oxygen with a KrF laser at 248 nm generates more ozone, contrary to the conventional chemistry which predicts that at this wavelength, all ozone will eventually be converted to oxygen. We have demonstrated that the reason that this occurs is that the generally ignored photodissociative channel in the Hartley band, that giving vibrationally excited oxygen and a ground state oxygen atom, is very important. Although only 10-15% of the dissociative process takes place by this pathway, as opposed to the major  $O(^1D) + O_2(a^1\Delta_g)$  channel, the effect of the presence of highly vibrationally excited oxygen is to act as an ozone source.

In the laboratory, this occurs because there is a strong Schumann-Runge oxygen absorption band in the neighborhood of 248 nm. The transition is that between ground state oxygen in the  $v=7$  vibrational level, and electronically excited  $B^3\Sigma_u^-$  oxygen in the  $v=2$  level. It turns out that ozone photodissociation at this wavelength generates a range of vibrational levels in oxygen, including  $v=7$ . Such molecules are excited by the same laser pulse to the  $B(2)$  level, from where they dissociate, resulting in one molecule of ozone being fragmented by two photons (not necessarily delivered simultaneously) into three atoms of oxygen. These atoms then recombine into three ozone molecules, and the process is a self-catalyzed ozone amplifier.

In the atmosphere, the same process has an advantage in that the solar continuum can in principle pump all vibrational levels that are produced during ozone photodissociation. In order to evaluate the possible effectiveness of the process as a stratospheric ozone source, two types of measurements are necessary; the determination of the distribution of vibrationally excited oxygen produced from 200-300 nm photodissociation of ozone, and the rate at which these molecules are quenched, presumably by oxygen. These measurements are currently being carried out.

- E. Slanger, T. G., L. E. Jusinski, G. Black, and G. E. Gadd, A new laboratory source of ozone and its potential atmospheric implications, *Science*, 241, 945, 1988.

## LABORATORY STUDIES OF TROPOSPHERIC AND STRATOSPHERIC REACTIONS

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### Objectives

The primary objective of this task is to study the rates and mechanisms of key elementary gas-phase reactions important in stratospheric and tropospheric chemistry. A secondary objective is to utilize high-resolution spectroscopic techniques in the ultraviolet, infrared and microwave regions to determine structural parameters and measure line positions and strengths of atmospheric molecules.

### Summary of Progress and Results

Considerable progress has been made in the last two years. Work has focused primarily on reactions important in polar stratospheric chemistry and the formation of the Antarctic ozone hole. The following studies in kinetics and spectroscopy were completed:

1.  $\text{BrO} + \text{ClO} \rightarrow \text{Products}$ . The reaction of ClO with BrO was investigated by two independent techniques, discharge flow-mass spectrometry and flash photolysis-UV absorption, over the temperature range 220-400 K and the pressure range 1-760 torr. Rate constants were determined for three product channels: a)  $\text{Br} + \text{ClOO}$ , b)  $\text{Br} + \text{OCIO}$  and c)  $\text{BrCl} + \text{O}_2$ . The results from the discharge flow and flash photolysis experiments were in good agreement and showed a significantly larger temperature dependence for the overall rate constant than previous work. In disagreement with previous studies, the channel forming BrCl was found to be significant (8%). The flash photolysis experiment also investigated the reaction,  $\text{Br} + \text{Cl}_2\text{O} \rightarrow \text{BrCl} + \text{ClO}$ , and the products of  $\text{Cl}_2\text{O}$  photolysis.
2.  $\text{ClO} + \text{ClO} + \text{M} \rightarrow \text{Cl}_2\text{O}_2 + \text{M}$ . The gas-phase recombination of ClO has been investigated under the conditions of pressure and temperature that prevail in the Antarctic stratosphere during the period of maximum ozone disappearance. The temperature and pressure dependence of the rate constant fall-off behavior was determined using the flash photolysis-ultraviolet absorption technique. Fall-off parameters were derived for  $\text{N}_2$ ,  $\text{O}_2$  and He bath gases. The measured rate constants were smaller than the previously accepted values by more than a factor of two. The results of the rate constant measurements were incorporated into a one-dimensional photochemical model to evaluate the relative rates of ozone depletion in the Antarctic stratosphere by the known catalytic cycles.
3. Molecular Structure of the ClO Dimer by Submillimeter Wave Spectroscopy. The products of the ClO self-reaction have been investigated between 220 K and 300 K by submillimeter wave spectroscopy. Chlorine peroxide,  $\text{ClOOCl}$ , has been definitively identified in the product mixtures. Below 240 K this species is found to be the predominant product. The complete spectrum between 415 and 435 GHz has been measured as well as selected transitions in the range 285 to 415 GHz. The rotational constants as well as a complete set of quartic centrifugal distortion constants have been determined. Structural parameters for the vibronic ground state have also been calculated.



4. Infrared Band Strength Measurement of the ClO Radical. High resolution ( $0.005\text{ cm}^{-1}$ ) FTIR spectra of the  $X^2\Pi_i-X^2\Pi_i$  (1-0) rovibrational bands of  $^{35}\text{Cl}^{16}\text{O}$  and  $^{37}\text{Cl}^{16}\text{O}$  have been obtained in 1 torr of helium carrier gas. After measuring the strengths of approximately 830 individual lines from several spectra, a total band strength,  $S_V = 13.1 \pm 1.1\text{ cm}^{-2}\text{ atm}^{-1}$ , and a first Herman-Wallis coefficient,  $\alpha = (4.12 \pm 0.62) \times 10^{-3}$ , were determined. The fundamental transition moment calculated from the band strength was  $-(3.9 \pm 0.2) \times 10^{-2}\text{ D}$ .

#### Journal Publications

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2. Lang, V. I., Sander, S. P. and Friedl, R. R., "Absolute Infrared Band Strength Measurement of the ClO Radical by FTIR Spectroscopy", *J. Mol. Spectrosc.*, **132**, 89 (1988).
3. Wahner, A., Ravishankara, A. R., Sander, S. P. and Friedl, R. R., "Absorption Cross Section of BrO Between 312 and 385 nm at 298 K and 225 K", *Chem. Phys. Lett.* **152**, 507 (1988).
4. Friedl, R. R. and Sander, S. P., "Kinetics and Product Studies of the Reaction ClO + BrO Using Discharge Flow-Mass Spectrometry", *J. Phys. Chem.*, **93**, 4756 (1989).
5. Sander, S. P. and Friedl, R. R., "Kinetics and Product Studies of the Reaction by Flash Photolysis-Ultraviolet Absorption", *J. Phys. Chem.*, **93**, 4764 (1989).
6. Anderson, J. G., Brune, W. H., Lloyd, S. A., Sander, S. P., Starr, W. L., Loewenstein, M. and Podolske, J. R., "Kinetics of O<sub>3</sub> Destruction by ClO and BrO Within the Antarctic Vortex: An Analysis Based on In Situ ER-2 Data", *J. Geophys. Res.*, in press.
7. Sander, S. P., Friedl, R. R. and Yung, Y. L., "Rate of Formation of the ClO Dimer in the Polar Stratosphere: Implications for Ozone Loss", *Science*, in press.
8. Birk, M., Friedl, R. R., Cohen, E. A., Pickett, H. M. and Sander, S. P., "The Rotational Spectrum and Structure of Chlorine Peroxide", *J. Chem. Phys.*, in press.

# KINETICS AND MECHANISMS OF STRATOSPHERIC CHLORINE RELEASE FROM CHLOROFLUOROMETHYL SPECIES

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## Research Objectives

The objective of this project is to conduct laboratory investigations leading to an understanding of the kinetics and mechanisms of Cl atom release from chlorofluorocarbons in the stratosphere. After the initial photolysis step, releasing the first Cl atom, peroxy radicals are formed rapidly by addition of O<sub>2</sub> to the chlorofluoromethyl photofragment. The ensuing reactions of the peroxy radical lead to photooxidation products that are formed by a complex and only partially understood mechanism. The work aims to reveal the steps in the mechanism and the pertinent kinetic parameters at stratospheric pressures and temperatures, and to assess the importance of these reactions with respect to inclusion in stratospheric models used for predicting O<sub>3</sub> depletion.

## Summary of Progress and Results

The kinetics of the termolecular reaction of CF<sub>2</sub>ClO<sub>2</sub> radicals with NO<sub>2</sub> was studied by flash photolysis of CF<sub>2</sub>ClBr in the presence of O<sub>2</sub> and NO<sub>2</sub> by means of time resolved mass spectrometry. A quadrupole mass spectrometer fitted with a Daly detector for ion counting was employed to detect the decay rates of the peroxy radicals via the CF<sub>2</sub>O<sub>2</sub> + (m/z = 82) fragment ion. An investigation of this reaction over the pressure range 1 to 10 torr and the temperature range 248K to 325K has now been completed.

During the course of this work, the signal to noise ration was vastly improved by adding cryogenic pumping to the ion source region, and replacement of our homemade axial geometry ionizer with a cross beam ionizer.

To assist in the analysis of this complex reaction system, a computer code (LSODE) was used to perform numerical simulations on the U of M CDC CYBER 170-877 computer. The calculations were done primarily to identify possible important secondary reactions, to verify assumptions made in analysis of the experimental data, and to insure that the reaction of interest was, in fact, isolated.

The formation of peroxy nitrates by addition of halomethylperoxy radicals to  $\text{NO}_2$  raises the question of the stratospheric stability of these species. We have built a continuous flow photoreactor for synthesis of halomethylperoxynitrates, and have been successful in obtaining pure samples of  $\text{CF}_2\text{ClO}_2\text{NO}_2$ . An investigation of its thermal decomposition is now underway, with an investigation of the photochemistry slated for the near future. The thermal decomposition studies are being done mass spectrometrically. A thermostatted batch reactor having a pinhole leak adjacent to the ion source permits decay of the reactant to be followed in real time.

Loss of reactant by flow through the pinhole should be corrected for. The flow is in the transition region, intermediate between bulk flow and Knudsen flow. Modeling this flow has proved difficult in the past, and our approach was to do empirical calibrations. During the course of the calibration work, we discovered that a simple interpolation formula gave a very accurate description of the net flow rates. Since this seems useful to others who use mass spectrometry for kinetics, we will publish the results.

Finally, in parallel with the experimental investigations, we redesigned the mass spectrometer sampling system, currently pinhole sampling, to a molecular beam sampling system. The machine shop work has been completed, and installation will be undertaken shortly.

### **Publications**

228.8 nm Photolysis of 1,1,1-Trichloroethane. G-Y. Chung and R. W. Carr, J. Photochem., accepted.

Kinetics of the Reactions of  $\text{CF}_2\text{ClO}_2$  Radicals with Nitrogen Dioxide. S. B. Moore and R. W. Carr, J. Phys. Chem., accepted.

Temperature Dependence of the Reaction of  $\text{CF}_2\text{ClO}_2$  Radicals with  $\text{NO}_2$ . F-S. Wu and R. W. Carr, to be submitted.

A Simple Interpolation Formula for Pinhole Flow in the Transition Regime. Q-J. Xiong and R. W. Carr, to be submitted.

# LABORATORY STUDIES OF CHEMICAL AND PHOTOCHEMICAL PROCESSES RELEVANT TO STRATOSPHERIC OZONE

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## RESEARCH OBJECTIVES

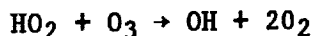
This program's purpose is to provide laboratory kinetic and thermodynamic data for stratospheric processes which will contribute to reducing the discrepancy between measurements and models in several areas: 1)  $\text{HO}_x$  chemistry including the reaction of  $\text{HO}_2$  with ozone at stratospheric temperatures, 2) the isotopic ozone anomaly in the mid-stratosphere including the mechanisms for "heavy" ozone formation, 3) upper stratospheric sodium chemistry investigating the possible impact of meteoric sodium compounds on chlorine-catalyzed ozone destruction, 4) the thermochemistry of stratospheric aerosols including measurements of equilibrium vapor pressures and solubilities of  $\text{HCl}$  in aqueous nitric acid and sulfuric acid particles. The results of these studies will provide data both for modeling the chemistry of ozone depletion and for designing improved field measurements of stratospheric constituents.

## SUMMARY OF PROGRESS AND RESULTS

### $\text{HO}_2$ Spectroscopy and Chemistry

Infrared line intensities in the three fundamental vibrational bands of the  $\text{HO}_2$  radical have been measured using a tunable diode laser coupled with a low pressure discharge-flow system. The integrated band strengths for the  $\nu_1$  ( $3400\text{ cm}^{-1}$ ),  $\nu_2$  ( $1400\text{ cm}^{-1}$ ) and  $\nu_3$  ( $1100\text{ cm}^{-1}$ ) bands are  $20 \pm 6$ ,  $58 \pm 16$ , and  $35 \pm 9\text{ cm}^{-2}\text{ (STP atm)}^{-1}$ . We have combined our individual linestrength results with an atmospheric transmission model in order to predict the optimal spectral regions for stratospheric measurements of  $\text{HO}_2$  by infrared absorption. Two sets of nearly coincident line pairs in the  $\nu_2$  band at  $1371.927$  and at  $1411.180\text{ cm}^{-1}$ , both of which have combined line intensities of  $1.5 \times 10^{-20}\text{ cm}^{-2}\text{ molecule}^{-1}\text{ cm}^{-1}$  at  $225\text{ K}$ , are relatively free from interference from other atmospheric absorption lines. These line intensities correspond to a fractional absorption in the stratosphere of  $1.3 \times 10^{-5}$  over a  $1\text{ km}$  path for an expected  $\text{HO}_2$  mixing ratio of  $200\text{ ppt}$  at  $30\text{ km}$  altitude.

We have also detected  $\text{H}^{18}\text{O}_2$  radicals with the TDL system and are currently studying the reaction



using isotopic labeling with  $^{18}\text{O}_2$  to eliminate interference from the back-reaction of  $\text{OH}$  product with  $\text{O}_3$  to reform  $\text{HO}_2$ . The emphasis of this study is on the reaction mechanism and product ( $^{18}\text{OH}$  or  $^{16}\text{OH}$ ) in the temperature range  $200$  to  $240\text{ K}$  relevant to the lower stratosphere.

### Ozone Isotope Studies

The isomeric distribution of  $^{18}\text{O}$  in heavy ozone produced in an electric discharge has been measured using infrared tunable diode laser spectroscopy to distinguish between  $^{16}\text{O}^{18}\text{O}^{16}\text{O}$  and  $^{16}\text{O}^{16}\text{O}^{18}\text{O}$ . Ozone samples with different levels of enhancement in heavy isotopes were analyzed simultaneously by molecular beam mass spectrometry and infrared absorption. Relative to total heavy ozone, the asymmetric  $^{16}\text{O}^{16}\text{O}^{18}\text{O}$  molecules are found to make up 4/5 of the enhancement. These results suggest that the mechanism responsible for heavy ozone enhancement in the stratosphere is strongly influenced by molecular symmetry in the  $\text{O} + \text{O}_2 + \text{M}$  recombination reaction.

These heavy ozone studies have been done in collaboration with J. Morton and K. Mauersberger at the University of Minnesota.

### Thermochemistry of Stratospheric Aerosols Compounds

Heterogeneous reactions on aerosol particles are responsible for the extreme springtime ozone depletions observed in the polar regions and may contribute to mid-latitude chlorine-ozone chemistry. The composition and chemistry of polar stratospheric clouds are crucial to the understanding of this phenomena.

We have initiated laboratory studies in order to determine the thermodynamic properties of the binary solids involving water with  $\text{HNO}_3$ ,  $\text{HCl}$ ,  $\text{HBr}$ , and  $\text{H}_2\text{SO}_4$ . A cryogenic chamber enclosing a multiple-pass infrared absorption cell has been designed, constructed and interfaced with a tunable diode laser spectrometer to measure vapor pressures of these molecules in equilibrium with ice-solid solutions and the relevant crystalline hydrates at stratospheric temperatures.

These studies are being conducted in collaboration with S. Wofsy and L. Fox from Harvard University.

### JOURNAL PUBLICATIONS

Mark S. Zahniser, Keith E. McCurdy, and Alan C. Stanton, "Quantitative Spectroscopic Studies of the  $\text{HO}_2$  Radical: Band Strength Measurements for the  $\nu_1$  and  $\nu_2$  Vibrational Bands," J. Phys. Chem. 93, 1065 (1989).

S.M. Anderson, J. Morton, and K. Mauersberger, "Laboratory Measurements of Ozone Isotopomers by Tunable Diode Laser Absorption Spectroscopy," Chem. Phys. Lett. 156, 175 (1989).

## PHOTOCHEMISTRY OF THE UPPER ATMOSPHERE

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### Objectives

To conduct laboratory studies of stratospheric photochemistry, including absorption cross sections, photolytic quantum yields, reaction mechanisms, and product distributions.

### Progress

A study of the chemical and UV spectral properties of the ClO dimer has been made. The dimer was prepared by static photolysis of Cl<sub>2</sub>-O<sub>3</sub> and Cl<sub>2</sub>-Cl<sub>2</sub>O mixtures in the temperature range 195-218K. The experiments were conducted both in the gas phase and in cryogenic solvents such as liquid CF<sub>4</sub>, CO<sub>2</sub>, and N<sub>2</sub>O. Accurate UV cross-sections in the wavelength range 190-400 nm were obtained in the gas phase and in the liquid media. No evidence was found for any dimer structure other than the symmetric form, ClOOC1. It was further shown that the dimer does not react with O<sub>3</sub> within this temperature range, and a rate constant upper limit of 1x10<sup>-19</sup> cm/molec-sec was established.

Photolysis of O<sub>2</sub>/H<sub>2</sub>O/CO mixtures at 184.9 nm was used to measure the steady-state ozone concentrations in these mixtures, which can be shown to depend only on the rate constant ratio

$$k(\text{HO}_2 + \text{O}_3) / k(\text{HO}_2 + \text{HO}_2)^{1/2}$$

The results were used to test the current best values, as recommended by the NASA Data Evaluation Panel, for the directly measured individual values for the two rate constants. The results showed that the recommended rate constants reproduce the observed ozone steady states to about 25%, which is within the stated error limits. The observed ozone concentration was higher than that predicted by the recommended rate constants. In a related series of experiments, tests were made for a pressure dependence of the OH+HO<sub>2</sub> reaction in the pressure range near one atmosphere, and none was found.

### Publications

1. "Yields of O<sub>2</sub>(a) and O<sub>2</sub>(b) in the H+O<sub>2</sub> Reaction System, and the Quenching of O<sub>2</sub>(b) by Atomic Hydrogen", Internat. J. Chem. Kin. 20, 915 (1988).
2. "UV Spectrum and Chemical Reactivity of the ClO Dimer", W. B. DeMore and E. T. Roux, paper presented at the Second International Conference on Chemical Kinetics, Gaithersburg, MD, July, 1989.

ATMOSPHERIC PHOTOCHEMISTRY  
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Objectives

This task is aimed at measuring in the laboratory rate constants and photochemical parameters for reactions which are potentially important in the stratosphere. The experiments involve both homogeneous and heterogeneous systems; the pressure and temperature ranges covered include those characteristic of the polar stratosphere. The systems under study include the photochemistry of  $\text{Cl}_2\text{O}_2$ ; the vapor pressures of HCl on ice-like substrates related to polar stratospheric clouds; and heterogeneous chemistry of  $\text{ClONO}_2$  on these substrates. The experimental techniques employed include laser photolysis, vacuum UV resonance fluorescence, FTIR and UV spectrophotometry, and mass spectrometry.

Summary of Program and Results

The quantum yield for the photodissociation of  $\text{Cl}_2\text{O}_2$  at 308 nm has been measured to be unity, within experimental error, for the production of Cl-atoms and ClOO radicals. The ClOO species has been found to be less stable than previously thought; it decomposes very fast yielding Cl-atoms and  $\text{O}_2$  molecules.

The solubility of HCl in various ices has been investigated. Pure water-ice readily absorbs HCl vapor, forming a hexahydrate, but only at HCl partial pressures above about  $10^{-5}$  torr. At lower partial pressures nitric acid trihydrate and impure ices have a stronger affinity for HCl, and these are the solid substrates that are expected to efficiently promote heterogenous chemical processes in the stratosphere.

Publications

1. Antarctic Stratospheric Chemistry of Chlorine Nitrate, Hydrogen Chloride, and Ice: Release of Active Chlorine, M. J. Molina, T. L. Tao, L. T. Molina, and F. C.-Y. Wang, Science, 238, 1253, 1987.
2. Interactions between HCl,  $\text{NO}_x$  and  $\text{H}_2\text{O}$ -Ice in the Antarctic Stratosphere: Implications for Ozone, J. Geophys. Res. 93, 2442, 1988.
3. The Antarctic Ozone Hole, M. J. Molina, Oceanus, 31, 47, 1988.
4. Primary quantum yields of  $\text{Cl}_2\text{O}_2$  photodissociation, M. J. Molina, A. Colussi, R. Schindler, L. T. Molina and T. L. Tso, in preparation, to be submitted to J. Phys. Chem.

A. *Title of Research Task:* STUDY OF THE ATMOSPHERIC CHEMISTRY OF NO<sub>y</sub> SPECIES

B. *Investigators and Institutions:* Jack G. Calvert, James A. Davidson, Christopher A. Cantrell, Richard E. Shetter, Anthony H. McDaniel, and Geoffrey S. Tyndall, Atmospheric Chemistry Division, National Center for Atmospheric Research, Box 3000, Boulder, CO, 80307.

C. *Abstract of Research Objectives:* Kinetic and spectroscopic studies will be made of several NO<sub>y</sub> species (NO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, NO<sub>2</sub>, CH<sub>3</sub>COO<sub>2</sub>NO<sub>2</sub>) which are important in the atmosphere and for which significant uncertainties in the reaction pathways remain. Rate constants for the following NO<sub>3</sub> reactions will be studied in flow and static systems using several spectroscopic and chemical techniques at a variety of temperatures and pressures characteristic of the troposphere and stratosphere: NO<sub>3</sub> + NO → 2NO<sub>2</sub> (1); NO<sub>2</sub> + NO<sub>3</sub> → NO + NO<sub>2</sub> + O<sub>2</sub> (2); NO<sub>2</sub> + NO<sub>3</sub> (+M) → N<sub>2</sub>O<sub>5</sub> (+M) (3), and N<sub>2</sub>O<sub>5</sub> (+M) → NO<sub>3</sub> + NO<sub>2</sub> (+M) (4). The nature of the primary processes and their quantum yields for NO<sub>3</sub> photodissociation as a function of wavelength and temperature will be determined: NO<sub>3</sub> + hν → NO<sub>2</sub> + O (5); NO<sub>3</sub> + hν → O<sub>2</sub> + NO (6). Several measurements which bear on the atmospheric chemistry of NO<sub>2</sub> will be made: a) the temperature dependence of the quantum yields and cross sections of NO<sub>2</sub> in the 397.9 to 420 nm range using low intensity laser beam excitation; b) measurements of the rate constant for the reaction: HO<sub>2</sub> + NO<sub>2</sub> → HONO + O<sub>2</sub> (7). New data related to the atmospheric properties of peroxyacetyl nitrate (PAN) will be determined: a) temperature dependence of the cross sections for PAN; b) rate constants for the suggested molecular rearrangements of PAN: CH<sub>3</sub>COO<sub>2</sub>NO<sub>2</sub> → CH<sub>3</sub>ONO<sub>2</sub> + CO<sub>2</sub> (8), and CH<sub>3</sub>COO<sub>2</sub>NO<sub>2</sub> → CH<sub>3</sub>CO + NO<sub>3</sub> (9). Finally studies will be undertaken to access the kinetics and products of the reaction of the NH<sub>2</sub> radical with O<sub>2</sub>.

D. *Summary of Progress and Results:*

Laser systems have been installed in a newly completed laser laboratory designed for these studies; rare gas, pulsed excimer and CW argon ion lasers are used to drive dye laser systems employed in these kinetic and spectroscopic studies.

Laboratory experiments were performed to measure the ratio of rate constants  $k_1/k_2$  for the reactions: NO<sub>3</sub> + NO → 2NO<sub>2</sub> (1) and NO<sub>2</sub> + NO<sub>3</sub> → NO + NO<sub>2</sub> + O<sub>2</sub> (2), respectively. This was accomplished through direct measurements of the nitric oxide and nitrogen dioxide concentrations in an N<sub>2</sub>O<sub>5</sub>/NO<sub>2</sub>/N<sub>2</sub> mixture. The NO was measured with NO/O<sub>3</sub> chemiluminescence, and the NO<sub>2</sub> was determined through long-path visible absorption spectroscopy. When the measured ratio is combined with recent measurements of  $k_1$ , then a value for  $k_2$  is calculated which is in reasonable agreement with other recent measurements from this laboratory.

A fast flow apparatus has been constructed to measure NO<sub>3</sub> rate coefficients by laser induced fluorescence. The NO<sub>3</sub> fluorescence is excited at 623 nm with light from the argon ion-pumped ring dye laser. The reaction of NO<sub>3</sub> with NO has been studied by following the kinetics of NO<sub>3</sub> in excess NO. At temperatures below 298 K the results are in good agreement with Hammer et al. (*J. Chem. Phys.*, 90, 2491-2496, 1986). At 298 K,  $k \approx 2.8 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>; E/R ≈ 1 -200 K. Experiments are in progress to establish the degree of curvature of the Arrhenius



plot for temperatures above 298 K. Experiments will be carried out using excess  $\text{NO}_3$ , detecting NO by chemiluminescence to check if any curvature of the Arrhenius plot observed in previous work results from secondary reactions of  $\text{NO}_3$ .

A temperature controlled (-80 to 200°C) reaction cell has been designed for use in planned kinetic studies of  $\text{N}_2\text{O}_5$  decay at high pressures (up to 400 psi). It is constructed of stainless steel with a 4 meter path length which will allow detection of the reactant gases by means of a visible, uv, and IR Fourier transform spectrometer or diode array spectrometer systems.

*E. Journal Publications on NASA Sponsored Research During 1988 and 1989*

1. The equilibrium constant for  $\text{N}_2\text{O}_5 \rightleftharpoons \text{NO}_3 + \text{NO}_2$ : absolute determination by direct measurement from 243 to 397 K, C. A. Cantrell, J. A. Davidson, A. H. McDaniel, J. G. Calvert, and R. E. Shetter, *J. Chem. Phys.*, **88**, 4997-5006, 1988.
2. The enthalpy of formation of dinitrogen pentoxide and nitrate free radical, A. H. McDaniel, J. A. Davidson, C. A. Cantrell, R. E. Shetter, and J. G. Calvert, *J. Phys. Chem.*, **92**, 4172-4175, 1988.
3. Visible-ultraviolet absorption cross sections for  $\text{NO}_2$  as a function of temperature, J. A. Davidson, C. A. Cantrell, A. H. McDaniel, R. E. Shetter, S. Madronich, and J. G. Calvert, *J. Geophys. Res.*, **93**, 7105-7112, 1988.
4. Temperature dependence of the atmospheric photolysis rate coefficient for  $\text{NO}_2$ , R. E. Shetter, J. A. Davidson, C. A. Cantrell, N. J. Bursynski, Jr., and J. G. Calvert, *J. Geophys. Res.*, **93**, 7113-7118 (1988).
5. Infrared absorption cross sections for  $\text{N}_2\text{O}_5$ , C. A. Cantrell, J. A. Davidson, A. H. McDaniel, R. E. Shetter, and J. G. Calvert, *Chem. Phys. Lett.*, **148**, 358-363, 1988.



## B. SPECTROSCOPY

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